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(54) Title: RECYCLABLE METATHESIS CATALYSTS

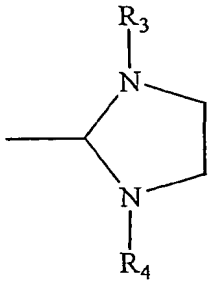
(57) Abstract: Hyghly active, recoverable and recyclable transition metal-based metathesis catalysts and their organometallic complexes including dendrimeric complexes are disclosed, including a Ru complex bearing a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene and styrenyl ether ligand. The heterocyclic ligand significantly enhances the catalytic activity, and the styrenyl ether allows for the easy recovery of the Ru complex. Derivatized catalysts capable of being immobilized on substrate surfaces are also disclosed. The present catalysts can be used to catalyze ring-closing metathesis (RCM), ring-opening (ROM) and cross metatheses (CM) reactions, and promote the efficient formation of various trisubstituted olefins at ambient temperature in high yield.

from the reaction mixture by silica gel chromatography in high yield and reused in subsequent C-C bond forming reactions. Kingsbury et al., *supra*. However, there are several shortcomings in the prior art recyclable metathesis catalyst, including that it is useful mostly for substrates that contain terminal alkenes. In certain cases, due to co-elution, isolation of the catalyst from the substrate is problematic.

## SUMMARY OF THE INVENTION

The present invention comprises highly active and recyclable transition metal-based metathesis catalysts, methods of making such catalysts and their use in metathesis reactions. The catalysts of the present invention are organometallic complexes of a transition metal comprising an organic ligand that permits recovery of the catalyst metal from the reaction mixture. The organometallic complexes of the invention can be in monomeric, polymeric and dendritic forms that are capable of promoting various forms of metathesis reactions in a highly efficient manner, and can be efficiently recoverd from the reaction mixtures and reused; they are therefore, recycleable. Unlike prior recoverable transition metal-based complexes, the catalysts of the present invention effect the efficient formation of trisubstituted alkenes and tetrasubstituted olefins through catalytic metathesis processes. The polymeric and dendritic catalysts of the invention offer the added advantage that they are more readily isolable. The present catalysts are extremely active (can be used to prepare tri- and tetra-substituted olefins), can be readily recovered and reused and leave little or no trace of toxic metal contamination within the product.

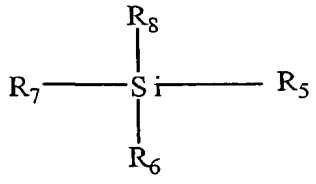
In one aspect, the invention comprises a composition comprising a monomeric catalyst having the following Formula I:



(II)

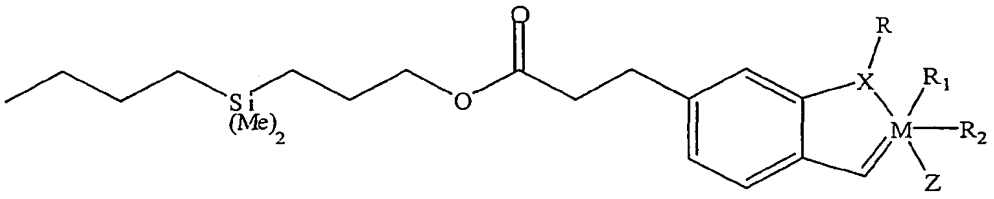
wherein $R_3$ and $R_4$ comprise he same or different aromatic ring moieties. In a currently preferred embodiment, R3 and $R_4$ both comprise 2,4,6-trimethylphenyl (mesityl) moieties.

In another aspect, the invention comprises dendritic catalyst structure having the following Formula III:



(III)

wherein $R_5$, $R_6$, $R_7$ and $R_8$ each comprises the following Formula IV:



(IV)

wherein:

M comprises a transition metal;

X comprises O, S, N or P;

R comprises an alkyl, alkenyl, alkynyl, aryl, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxy carbonyl, alkylamino, alkylthio, alkylsulfnyl, alkylsulfinyl; each optionally submitted with an alkyl, halogen, aryl or heteroaryl moiety;

Immobilization of catalysts of the invention to an inorganic monolithic gel provides the following advantages over immobilization of such catalysts on conventional solid phases such as organic polymer beads : (1) overcomes limitations of organic polymer beads such as variable swelling and shrinking in different media, often resulting in reduction of catalytic activity (2) precludes the addition of significant volumes of solvents needed for recovery of beads bound to the catalyst, a necessity that seriously limits the utility of recoverable surface immobilized catalysts, thereby detracting from the practicality of such an approach and rendering it more costly and environmentally less friendly. (3) The high porosity characteristic of inorganic gels translates to a substantially large interfacial surface area (typically 300-1000 $m^2/g$), rendering such materials ideal for immobilization of catalysts of the invention. (4) Gelation occurs after a sol is cast into a mold; it is, therefore, possible to tailor the gel samples to a desired shape or even function.

In another preferred embodiment, the surface immobilized catalysts of the present invention is an integral part of the reaction apparatus itself, thus obviating the need for a filtration step to recover the catalyst after completion of metathesis processes. Processes of the present invention are, therefore, rendered operationally simple from the standpoint of both execution and work-up.

The recyclable catalysts of the present invention are substantially more active than prior art recyclable metathesis catalysts. The transition metal-based monomers and dendrimers of the present invention are easily characterizable and serve as homogeneous metathesis catalysts that are highly active and allow for significantly more facile catalyst recovery compared to prior art catalysts.

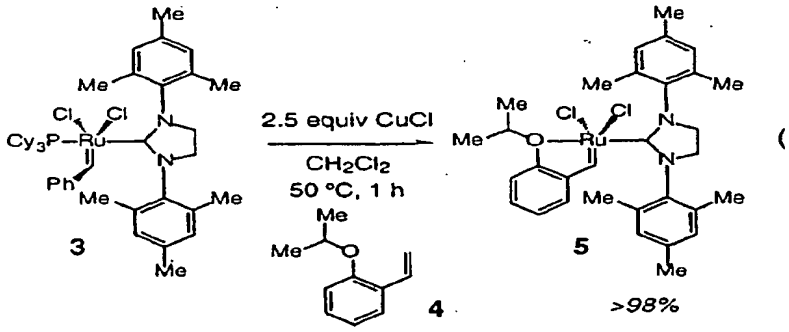
## BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows two prior art ruthenium catalysts: (1) is a recoverable complex of ruthenium with an isopropoxystyrene and a phosphine moiety, and (2) is a benzylidene catalyst.

The present catalysts can be recovered from the reaction mixture by any technique suitable for recovering or separating organometallic complexes, including chromatography or filtration. For example, the monomeric or dendritic catalysts may be separated form the reaction mixture by silica gel chromatography. If the catalyst is attached to a solid phase, as described below, then the catalyst can be recovered by separating the solid phase from the reaction mixture by simple filtration.

**Monomeric complexes.** In one aspect, the present invention provides monomeric catalysts having the structure shown as Formula I. Monomeric catalysts having Formula I can be prepared according the procedures shown in Equation 1 below, in Examples 1-10, or via other synthetic routes that would be readily ascertainable by those skilled in the art.

The structure shown as Formula 5 in Equation 1 below comprises a currently preferred embodiment of the present invention.




**Equation 1**

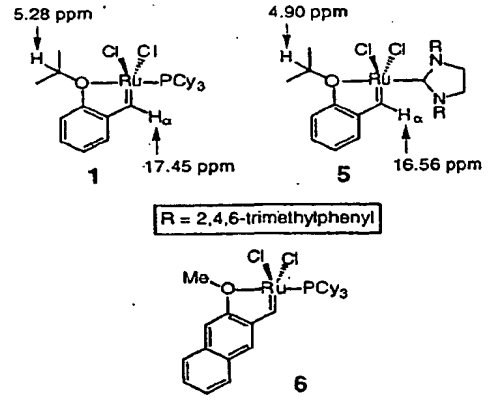
**Synthesis of Formula 5.** The catalyst of Formula 5 was synthesized and characterized, and its reactivity and recyclability were determined. It was determined that the saturated imidazolin-2-ylidene and unsaturated imidazol-2-ylidene carbene ligands accelerated the metathetic activity of Ru-based complexes. As depicted in Equation 1, treatment of compound 3 with 2.5 equivalents CuCl and 0.97 equivalents of compound 4 in $CH_2C1_2$ at 40°C delivers the

| | | | |
|---|---|---|---|
| Ru(1 )-C(2) | 1.981(5) | Ru(1 )-Cl(2) | 2.340(12) |
| Ru(1 )-0(1) | 2.261(3) | C(2)-N(1) | 1.351(6) |
| | | C(2)-N(2) | 1.350(6) |

| Bond angles (deg) | | | |
|---|---|---|---|
| C(1 )-Ru(1 )-0(1) | 79.3(17) | 0(1 )-Ru(1 )-Cl(1) | 86.9(9) |
| C(1 )-Ru(1 )-C(2) | 101.5(14) | 0(1 )-Ru(1 )-Cl(2) | 85.3(9) |
| C(2)-Ru( 1 )-0(1) | 176.2(14) | C(2)-Ru(1 )-Cl(1) | 96.6(12) |
| C(1 )-Ru(1 )-Cl(1) | 100.2(15) | C(2)-Ru(1 )-C(2) | 90.9(12) |
| C(1 )-Ru(1 )-Cl(2) | 100.1(15) | Cl(1 )-Ru(1 )-Cl(2) | 156.5(5) |
| | | N(1 )-C(2)-N(2) | 106.9(4) |

Comparison of the $^1$H NMR spectra of prior art compound 1 (shown in Figure 1) and Formula 5 shows some of the structural attributes of these complexes. As illustrated in Scheme 1, there are two distinct chemical shift changes in the 400 MHz $^1$H NMR spectra of Formula 5 and compound 1.

**Scheme 1**

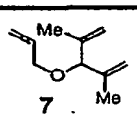
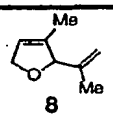
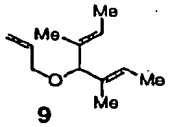
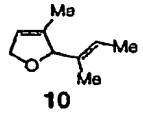
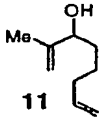
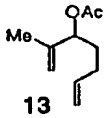
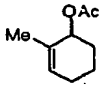
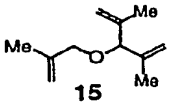
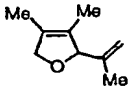
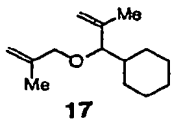
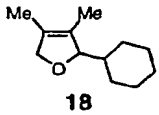


followed by the addition of 10 mol % 4 and addition stirring for 1 h, leads to the formation of 12 and 5 in 98% and 82% yields, respectively (after silica gel chromatography).

(2) Catalyst loading lower than 5 mol % is sufficient. As exemplified by the reaction in entry 2, catalytic RCM can readily proceed to completion with only 1 mol % Formula 5 catalyst. As another example, catalytic RCM of 7 occurs within 10 mm at 22°C in the presence of 1 mol % of 5 to afford 8 in 73% isolated yield (>98% conv); recovered 5 is obtained in 92% yield after chromatography.

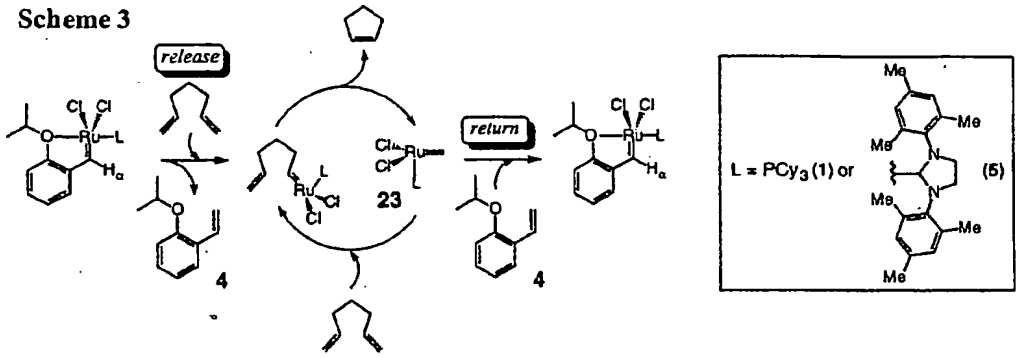
As the reaction in entry 5 of Table 2 indicates, tetra-substituted olefins can also be obtained through catalytic RCM promoted by the catalyst of Formula 5.

**Table 2.** Ring-Closing Metathesis of Acyclic Dienes by Ru Complex 5 [a]

| entry | substrate | product | time | conv (%) | product yield (%) [b] | catalyst recovery (%) [b] |
|---|---|---|---|---|---|---|
| 1 |  7 |  8 | 10 min | >98 | 82 [c] | 98 |
| 2 |  9 |  10 | 20 min | >98 | 87 | 98 |
| 3 |  11 |  12 | 2 h | >98 | 75 | 95 |
| 4 |  13 |  14 | 1.5 h | >98 | 82 | >98 |
| 5 |  15 |  16 | 44 h | 42 | 38 | 81 |
| 6 |  17 |  18 | 30 min | 70 | 65 | 60 |

Scheme 3 shows the release/return mechanism by which the present monomeric catalysts function as metathesis catalysts. As shown therein, a diene substrate probably first reacts with the initial Ru complex to remove the transition metal from the styrene ligand and "release" the styrene ether 4. Upon consumption of the diene, the active Ru-carbene reacts with the previously occupied styrenyl ether to cause reformation or "return" of the initial complex.

**Scheme 3**



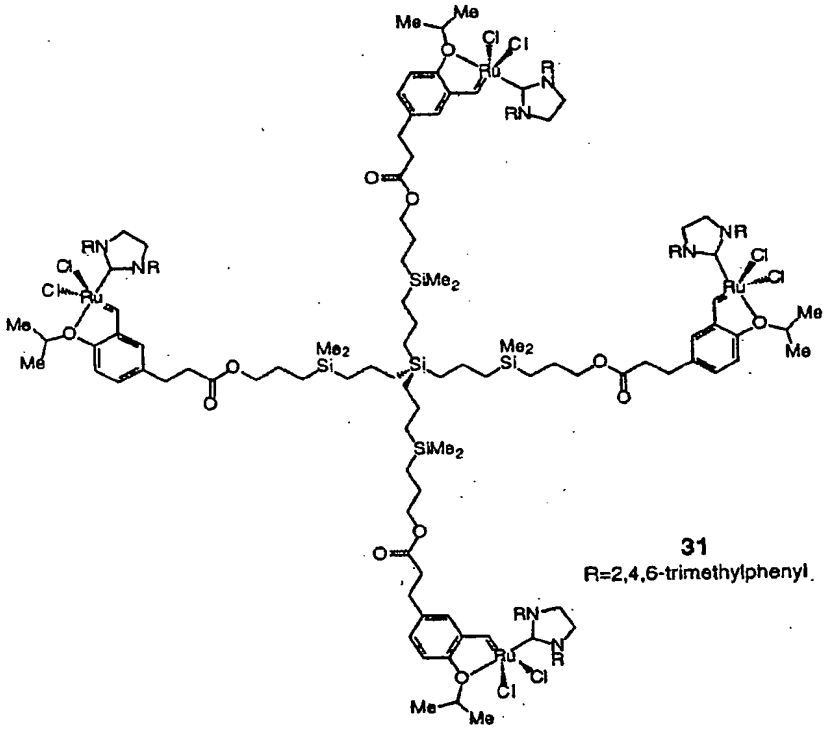

**Dendritic complexes.** In another aspect, the present invention provides dendritic catalysts having the structure shown as Formula III. Dendritic catalysts having Formula III can be prepared according the procedures described below, in Examples 11-16, or via other synthetic routes that would be readily ascertainable to these skilled in the art.

The structures shown as Formulae 30 and 31 below comprise currently preferred embodiments of the present invention.

Dendritic complexes, due to their different polarity compared to the monomeric species, generally can be more easily separated from reaction products. With dendrimers, it is possible to gauge more rigorously the efficiency with which the active metal-carbene leaves the ligation site and returns to the catalyst macromolecule. In addition both the release of the metal center from the styrenyl ligand (initiation) and the return of the active metal to the initial site (recovery), which is shown in Scheme 3 above, are more efficient with the more accessible and exposed terminal sites within the dendrimer structure.

of the dendrimer backbone by a platinum (Pt)-catalyzed hydrosilation / alkylation / hydroboration sequence (27 28 29). Coupling of 29 with four equiv 26, followed by incorporation of the Ru center through treatment with 2 in the presence of CuCl affords the desired 30 as an air stable brown solid (mp = 92-98 °C dec.).

Another preferred Ru-containing dendrimer, Formula 31, can be prepared as an air stable dark green solid by the same sequence of reactions as shown in Scheme 4, except that the last step involves treatment of the vacant dendritic structure with 4.3 equiv 3 and 4.6 equiv CuCl in $CH_2Cl_2$ for 10 mm (55% yield; mp = 114-117°C dec).

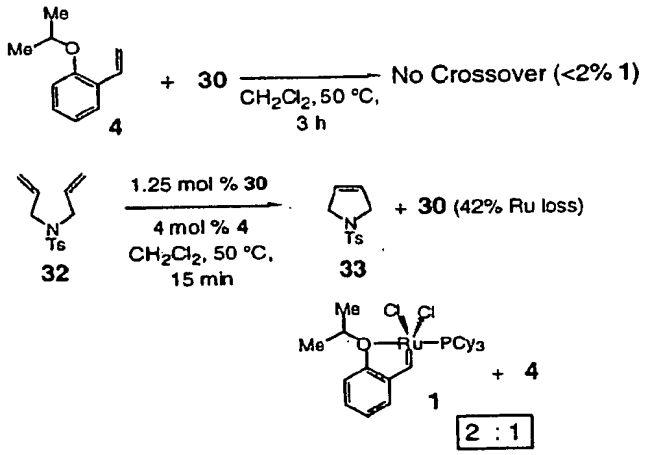


**31**
R=2,4,6-trimethylphenyl.

**Catalytic RCM, ROM and CM Promoted by Dendritic Catalysts of Formulae 30 and 31.** Table 3 below illustrates the use of the present dendritic catalysts in a RCM reaction. As shown in Table 3, treatment of diene 32 with 1.25 mol % of 30 (5 mol % Ru) leads to efficient and catalytic RCM. The desired product (33) is first isolated in 99% yield by silica gel chromatography through elution with $CH_2Cl_2$ subsequent wash of the silica with Et2O leads to the isolation of the dendritic catalyst (>98% mass balance). Recovered 30 was analyzed by 400

dendrimer complex can be easily re-metaflated upon treatment with the appropriate equivalents of 3 and CuCl in $CH_2Cl_2$. The dendritic complex remains active even after nearly 50% of the Ru content has been depleted (see cycle 6 in Table 3). This level of reactivity may be attributed, at least partially, to the fact that 30 (similar to monomeric catalysts 1 and 5) releases a highly active mono-phosphine Ru complex into the solution. In the absence of a second equivalent of $PCy_3$ that can re-coordinate to Ru and retard its catalytic activity (which is the case when 2 or 3 are used as catalysts), and since styrene ethers probably do not kinetically re-associate with Ru as efficiently as $PCy_3$, even a small amount of Ru release can lead to substantial amounts of metathesis activity.

**Scheme 5**




Metal crossover experiments were carried out as depicted in Scheme 5. Treatment of compound 4 with dendritic Ru complex of Formula 30 results in little or no metal crossover (<2% 1 formed by 400 MHz $^1$H NMR analysis). The amount of Ru bound to the dendritic vs monomeric ligands is readily determined by the chemical shift difference in the $^1$H NMR spectra of the corresponding carbene CH (Ru=C(H)). When diene substrate 32 is treated with 1.25 mol % fully loaded 30 and 4 mol % 4, RCM product 33 is obtained within 15 mm. However, recovered 30 bears 42% less Ru, compared to 13% metal reduction when the reaction is carried

corresponding monomer 5, dendrimer 31 can be easily separated from 20 and recovered in 90/s yield (8% Ru loss). The transformation in **Scheme 6** indicates that 31 effectively promotes catalytic ROM / CM reactions as well, and as before, it can be recovered readily and in good yield (>98% trans olefins in 22 and 34, as judged by 400 MHz $^1$H NMR analysis). Thus, dendritic catalyst 31 retains the high activity of monomeric 5 and provides the valuable practical advantage of being readily separable from metathesis products.

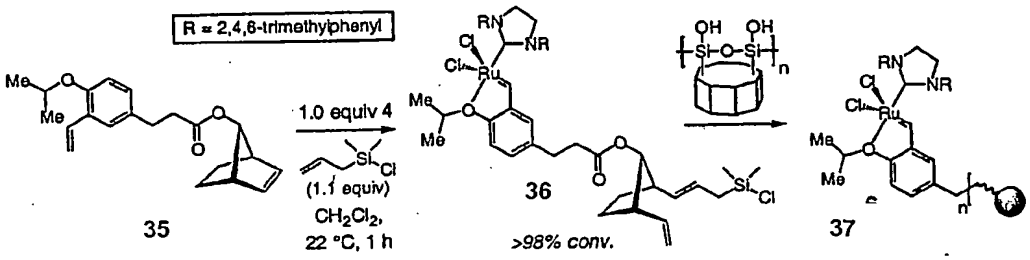
Similar to monomeric 5, lower loadings of 31 are sufficient for efficient catalytic metathesis. As an example, when triene 7 is treated with 0.25 mol % 31 ($CH_2Cl_2$, 22°C) for 10 mm, RCM adduct 8 is formed with >98% cony. In addition to dihydrofuran 8, isolated in 84% yield, recovered 31 is obtained in 88% yield after silica gel chromatography (22% Ru loss).

**Immobilization of the Catalysts on a Solid Phase.** The present catalysts can be attached to or immobilized on a solid support for use in metathesis reactions. Solid phases which can be used include, for example, metals (including magnetic media), glass, polymers, ceramics or other inert substances that will not affect the reaction. The solid phase may be in any form useful for carrying out the particular reaction, including particles, beads, rods, plates, fibers, filters, etc. Methods for attaching organometallic catalysts to solid supports and using them in metathesis reactions are known in the art. One method for attaching the preferred monomeric catalyst of the present invention to a polymer substrate is described in Example 19.

The catalysts of the present invention can be immobilized with retention of all the ligand environment characteristics responsible for its high activity. In one embodiment, the immobilized catalyst is immobilized on the solid support in a manner such that the support is a catalyst carrier. In this embodiment, the metathesis substrate releases the active metal carbene from the polymer, the complex promotes several cycles in solution, and is again trapped by the support so that it can be easily retrieved and reused. In other words, the present immobilized

sol-gel monoliths such as, for example, glass monolithic gel with about 200 Å pore size to the reaction mixture, followed by stirring for 96 h at 40 °C. After extensive washing with $CH_2Cl_2$ and drying in vacuo, bright green glass pellets of surface immobilized catalyst **37** are recovered.

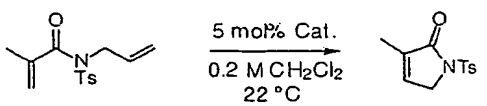
In other preferred embodiments, surface immobilized catalysts **38** and **39** shown in **Scheme 7** are obtained in an analogous fashion from the corresponding norbornene substrates. Surface immobilized catalysts **35, 36** and **37** were evaluated for catalytic activity, recovery and recyclability.




**Scheme 7**

All surface immobilized catalysts of the present invention show good activity in catalyzing metathesis reactions. **Table 4** shows efficiency of immobilized catalysts **37, 38** and **39** carried through iterative rounds of ring-closing metathesis (RCM) of acrylic amide **40** to yield **41**. The catalyst loading for each of these transformations was determined by the mass increases that accompany functionalization of the gel surface. Relative reaction rates of three catalysts were assessed by stopping the reaction prematurely during the third round of RCM, at a point where TLC analysis still showed the presence of a small amount of starting material. Spectroscopic analysis of the (400 MHz $^1$H NMR) unpurified reaction mixture (97-100% conversion, Round 3, Table 4) indicates that reaction efficiency of all three catalysts tested are equivalent.

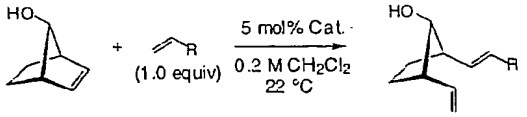
**Table 4**. Utility of Immobilized Catalysts in catalyzing RCM




**40** **41**

donor olefins, including highly electron-rich olefins such as vinylferrocene. As shown in **Table 5**, productive metathesis for three additional rounds of norborneol **42** occurred in <1 h to yield ring-opened compound **43**. The Ru-containing impurities, as well as the product of the previous RCM reaction **39** could not be detected by NMR spectroscopy (400 MHz $^1$H NMR analysis) of the corresponding unpurified reaction product mixtures.

**Table 5**. Efficiency of Recycled Catalysts in catalyzing ROCM




**42** **43**

| Catalyst | R=Ph<br>Rounds 5 (40 min) | R = n-hexyl<br>Round 5 (40 min) | R – Ferrocene<br>Round 7 (40 min) |
|---|---|---|---|
| 37 | >98% conv | >98% conv | >98% conv |
| 38 | >98% conv | >98% conv | >98% conv |
| 39 | >98% conv | >98% conv | >98% conv |

In addition to attaching the catalyst to a substrate such as an organic polymer bead that necessitates an additional filtration step to isolate the product from catalyst, the catalysts of the invention may be immobilized on the surface of a reaction vessel. In a preferred embodiment, the catalyst metal complex is immobilized to an integral part of the reaction apparatus itself, for example, a glass round-bottom reaction flask, a magnetic stir bar, or other component used to carry out the reaction. Catalysts of the present invention may also be attached to highly porous glass monoliths, which can be synthesized and manipulated from readily available materials.

Preferably, the linker moiety used to bind the metal complex to the solid support should be chemically inert under the reaction conditions and form a non-labile link between the metal complex and support. In one embodiment, as shown in **Scheme 7**, the present catalysts are

shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: 77.00 ppm; $CD_3CN$: 1.19 ppm). $^{31}P$ NMR spectra were recorded on a Varian Gemini 2000 (162 MHz) spectrometer with complete proton decoupling. The chemical shifts of the phosphorus resonances were determined relative to phosphoric acid as an external standard ($H_3PO_4$: δ 0.0 ppm).

All reactions were carried out under an atmosphere of dry Ar in oven- (135°C) and flame-dried glassware with standard Schlenk or vacuum-line techniques. In most instances, solid organometallic compounds were purified and recovered in air and later stored in a drybox under an atmosphere of argon. $(PCy_3)Cl_2RuCHPh$ (**Formula 2**) was prepared according to literature procedures.[30] (4,5-dihydrolMES)$(PCy_3)Cl_2Ru$=CHPh (**Formula 3**) and its requisite starting materials were prepared by a modification of the published method[31] (see below for further details). 2-isopropoxystyrene was prepared by alkylation and Wittig olefination. All other materials were obtained from commercial sources and purified before use. Tetrahydrofuran, diethyl ether, benzene, and toluene were distilled from sodium metal/benzophenone ketyl. Dichloromethane, pentane, hexanes, 2-propanol, triethylamine, and ethanol were distilled from calcium hydride under Ar. Methanol was distilled over Mg under Ar. 2,4,6-trimethylaniline was vacuum distilled. Triethyl orthoformate (Aldrich) was distilled from $MgSO_4$ under reduced pressure. 3-(4-Hydroxyphenyl)-propionic acid (Aldrich) was recrystallized from water. 2-Iodopropane (Aldrich) was distilled from $MgSO_4$ under argon. Dimethylformamide (Fisher) was stored over 4A molecular sieves prior to use. Tributyl(vinyl)tin (Aldrich) was vacuum distilled from $MgSO_4$. Allylmagnesium bromide was freshly prepared from distilled allyl bromide (Aldrich) and Mg turnings (Strem) and titrated before use. Silicon tetrachloride (Strem) was distilled under argon. Chlorodimethylsilane (Aldrich) was distilled under argon. 9-Borabicyclo[3.3.1]nonane (9-BBN) was freshly prepared from distilled 1,5-cyclooctadiene (Aldrich), borane-dimethylsulfide complex (Aldrich), and anhydrous dimethoxyethane (Aldrich, distilled from sodium metal/benzophenone ketyl).[32] 4-Dimethylaminopyridine (DMAP)

yellow solution was dried over $MgSO_4$, filtered, and concentrated to a yellow-orange solid residue. The unpurified product was recrystallized from anhydrous methanol (for every 10 g, 850-900 mL of MeOH was required for complete dissolution at reflux). After slow cooling to 22 EC followed by subsequent storage of the sample at -20 °C for 12 h, long canary yellow crystals formed. The product was recovered by vacuum filtration, washed with pentane, and dried under high vacuum (7.40 g, 25.3 mmol, 86%). IR (NaCl): 3005 (m), 2946 (s), 2916 (s), 2854 (m), 2725 (w), 1617 (s), 1595 (w), 1476 (m), 1438 (w), 1374 (m), 1265 (m), 1202 (s), 1141(m), 1031 (w), 850 (s), 780 (m), 739 (s), 705 (w), 609 (w). $^1$H NMR (400 MHz, $CDC1_3$): 8.12 (s, 2H, NCH), 6.93 (s, 4H, aromatic CH), 2.31 (s, 6H, mesityl *p*-$CH_3$), 2.18 (s, 12H, mesityl *o*-$CH_3$). $^{13}$C NMR (100 MHz, $CDCI_3$): δ163.31, 147.29, 134.13, 128.86, 126.44, 20.83, 18.28. HRMS Calcd for $C_{20}H_{23}N_2$: 292.1861 $(M-H)^{+\cdot}$ Found: 291.1862. Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27.Found: C, 81.99; H, 8.12.

**Example 2: Synthesis of ((2,4,6-Trimethylphenyl)NHCH$_2$)$_2$.** The bis(imine) ((2,4,6-trimethylphenyl)NCH) (7.30 g, 25.0 mmol) was suspended in 250 mL of MeOH in a 500 mL round-bottom flask. Several crystals of bromocresol green were added as a pH indicator and the mixture was cooled to 0 °C. $NaCNBH_3$ (10.0 g, 159 mmol, 6.4 equiv) was added to the reaction mixture in one portion as a solid. Vigorous bubbling was observed and the reaction mixture turned a deep blue-green color (alkaline pH). After 10 mm concentrated HCI was added dropwise to the mixture, restoring its original yellow color. Additional reduction slowly occurred, causing the mixture to again become basic. The acidification process was repeated (typically two more times) until the yellow color persisted. The reaction mixture was warmed to 22 °C and stirred for 1 h. A solution of 2 M KOH was added dropwise until the mixture was weakly alkaline (pH = 8-9). The mixture was then diluted with water (300 mL), transferred to a separatory funnel, and washed three times with $Et_2O$ (500 mL). The combined organic layers were washed with 800 mL of saturated solution of sodium chloridc, dried over MgSO4, filtered, and concentrated into a yellow oil. Silica gel chromatography (TLC R*f*= 0.32 in 4:1 pentane:

**Example 4: Synthesis of (4,5-dihydrolMES)($PCy_3$)Cl2Ru=CHPh (formula 3).** The ligand salt 1,3-dimesitylimidazolinium tetrafluoroborate (2.94 g, 7.46 mmol, 1.2 equiv) was suspended in 50 mL of THF in a 250 mL round-bottom flask. This mixture was then treated with a solution of potassium *tert*-butoxide (840 mg, 7.49 mmol, 1.2 equiv) in 50 mL of THF via cannula at 22 EC. This mixture was immediately cannula transferred (20 mL THF used as rinse) to a second vessel containing a solution of ($PCy_3$)$Cl_2$Ru=CHPh (2) (5.01 g, 6.09 mmol, 1.0 equiv) in 100 mL of benzene (additional stirring of the ligand salt mixture at 22 °C prior to exposure to the Ru-carbene often resulted in incomplete conversion to the desired product). The resulting mixture was refluxed at 80 EC for 30 mm and then cooled to 22 °C. All manipulations from this point forward were carried out in air with reagent-grade solvents. The solvents were removed at reduced pressure, leaving a red-brown solid residue. The crude residue was dissolved in a minimal volume of 9:1 hexanes: $Et_2O$ and loaded onto a wide plug of silica gel. Elution with the same solvent system slowly removed a pink-red band of the desired product from the column. Concentration of the product fractions in vacuo removed the more polar and volatile $Et_2O$ and resulted in spontaneous precipitation of the catalyst from hexanes as a cranberry red, microcrystalline solid (3.78 g, 4.45 mmol, 73%). These crystals were dried under high vacuum. IR (NaCl): 3057 (m), 3039 (m), 3015 (m), 2927 (s), 2850 (s), 1608 (w), 1479 (s), 1446 (s), 1421 (s), 1380 (m), 1328 (w), 1266 (s), 1243 (m), 1205 (w), 1174 (m), 1129 (w), 1036 (w), 1005 (m), 909 (m), 849 (m), 737 (s), 703 (m), 687 (m), 624 (w), 578 (w). $^1$H NMR (300 MHz, $CDCl_3$): δ 19.13 (s, lH, Ru=CHAr), 7.35 (dd, $J$ = 7.8, 7.0 Hz, 2H, aromatic CH), 7.09 (m, 3H, aromatic CH), 7.01 (s, 4H, mesityl aromatic CH), 3.98 (s, 4H, $N(CH_2)_2N$), 2.80-0.70 (m, 33H, $P(C_6H_{11})_3$), 2.31 (s, 12H, mesityl *o*-$CH_3$), 1.90 (s, 6H, mesitylp-$CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 293.40, 220.29 (d, $^J$CN = 76.2 Hz), 151.16, 151.11, 138.27, 137.49, 137.08, 135.06, 129.77, 127.78, 51.64 (d, $^J$CN = 71.9 Hz), 31.30 (d, $^J$*PC* = 15.6 Hz), 27.68 (d, = 9.8 Hz), 26.07, 21.09, 20.86, 19.88. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 161.90 (s, $PCy_3$). Anal. Calcd for $C_{46}H_{65}Cl_2N_2PRu$: C, 65.08; H, 7.72. Found: C, 65.18; H, 7.71.

$C_{31}H_{38}Cl_2N_2O^{99}Ru$: 623.1421 Found: 623.1411. Anal. Calcd for $C_{31}H_{38}Cl_2N_2ORu$: C, 59.42; H, 6.11; Cl, 11.32; N, 4.47. Found: C, 59.28; H, 6.35; Cl, 11.36; N, 4.12.

**Example 6: Synthesis of Isopropyl-1-(*p*-hydroxyphenyl)propionate.** Through a stirring solution of 3-(4-hydroxyphenyl) propionic acid (24) (5.00 g, 30.1 mmol) in 2-propanol (167 mL, 72.0 equiv) was bubbled anhydrous HCl for 50 mm. The flask was sealed under Ar and stirred for 12 h at 22 °C. The solvent was removed under reduced pressure with gentle heating, leaving a thick, colorless oil. Removal of residual 2-propanol under high vacuum at 22 °C resulted in spontaneous precipitation of the desired product as a bright white crystalline solid (6.12 g, 29.4 mmol, 98%). IR (NaCl): 3412 (br), 3024 (w), 2981 (m), 2930 (w), 2873 (w), 1712 (m), 1613 (s), 1595 (m), 1519 (s), 1449 (m), 1377 (s), 1298 (m), 1266 (s), 1225 (s), 1149 (m), 1108 (s), 904 (m), 837 (m), 820 (m), 609 (m). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, J 8.4 Hz, 2H, aromatic CH), 6.74 (d, $J$ = 8.4 Hz, 2H, aromatic CH), 5.80 (s, lH, ArOH), 5.00 (septet, $J$ = 6.3 Hz, lH, $(CH_3)_2CHO$), 2.87 (t, $J$ = 7.6 Hz, 2H, $CH_2CO_2iPr$), 2.57 (t, $J$ = 7.6 Hz, 2H, $ArCH_2$), 1.20 (d, $J$ = 6.3 Hz, 6H, $(CH_3)_2CHO$). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 172.97, 154.04, 132.19, 129.28, 115.19, 68.07 (d, Joc= 9.8 Hz), 36.64, 30.23, 21.85. HRMS Calcd for $C_{12}H_{16}0_3$: 208.1099. Found: 208.1099. Anal. Calcd for $C_{12}H_{16}0_3$: C, 69.21; H, 7.74. Found: C, 69.43; H, 7.88.

**Example 7: Synthesis of Isopropyl-1 -(*p*-isopropoxyphenyl)propionate (25).** A solution of isopropyl-I -(*p* hydroxyphenyl)propionate (0.822 g, 3.95 mmol) in THF (10 mL) was treated via cannula with a suspension of sodium hydride (104 mg, 5.92 mmol, 1.1 equiv) in THF (10 mL) at 0 °C. After gas evolution had subsided, DMF (20 mL) and 2-iodopropane (0.40 mL, 4.0 mmol, 1.0 equiv) were syringed into the reaction mixture. The resulting suspension was stirred at 22 °C for 6 hours, at which time additional sodium hydride (71.0 mg, 2.96 mmol. 0.75 equiv) in THF (5 mL) and 2-iodopropane (0.30 mL, 3.0 mmol, 0.75 equiv) were added. This procedure was repeated if necessary until no starting material could be detected by TLC analysis

chromatography (TLC $R_f$= 0.23 in 10:1 hexanes:$Et_2O$) to deliver the product as a colorless oil (1.40 g, 4.25 mmol, 98%). Crucial to the success of this reaction is this use of *exactly* 1.0-1.1 equiv of bromine; an excess of the reagent leads to dibrominated adducts. If these impurities are generated, a $CH_2Cl_2$/pentane solvent system must be used as eluant to effect purification of the desired product on silica gel (TLC $R_f$= 0.30 in 3:2 $CH_2Cl_2$:pentane). The halogenated solvent mix also promotes a facile separation of the product and the starting material (25) in the event that the reaction does not proceed to completion (<1.0 equiv $Br_2$). IR (NaCl) 2979 (m), 2936 (w), 1729 (s), 1604 (w), 1493 (s), 1384 (m), 1373 (m), 1281 (m), 1253 (s), 1240 (m), 1180 (m), 1140 (m), 1109 (s), 1046 (w), 954 (m), 812 (w). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J*= 2.2 Hz, lH, aromatic CH), 7.06 (dd, *J* = 8.4, 2.2 Hz, lH, aromatic CH), 6.83 (d, *J* = 8.4 Hz, lH, aromatic CH), 4.96 (septet, *J* = 6.2 Hz, 1H, $(CH_3)_2CHO_2C$), 4.50 (septet, *J* = 6.2 Hz, 1H, $(CH_3)_2CHOAr$), 2.85 (dd, *J* = 7.7, 7.3 Hz, 2H, $CH_2CO_2iPr$), 2.55 (dd, *J* = 7.7, 7.3 Hz, 2H, $ArCH_2$), 1 .36 (d, *J* = 5.9 Hz, 6H, $(CH_3)_2CHOAr$), 1.20 (d, *J* = 6.6 Hz, 6H, $(CH_3)_2CHO_2C$). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 172.06, 152.84, 134.36, 133.09 (d, $J_{OC}$= 7.3 Hz), 128.03, 115.98, 113.63, 72.34 (d, $J_{OC}$= 3.9 Hz), 67.80 (d, $J_{oc}$= 12.2 Hz), 36.29, 29.90, 22.15 (d, $J_{oc}$ 2.4 Hz), 21.89 (d, $J_{oc}$ 3.4 Hz). HRMS Calcd for $C_{15}H_{21}BrO_3$: 328.0674. Found: 328.0671. Anal. Calcd for $C_{15}H_{21}BrO_3$: C, 54.72; H, 6.43. Found: C, 54.84; H, 6.43.

**Example 9: Synthesis of Isopropyl-1 -(*p*-isopropoxy-*m*-vinylphenyl)propionate.** $Pd(PPh_3)_4$ (166 mg, 0.144 mmol, 3 mol %) and 2,6-di-*tert*-butyl-4-methylphenol (1 mg, 0.005 mmol) were weighed into a 50 mL pear-shaped flask in a glove box and dissolved in 25 mL of dry toluene. This solution was transferred through a cannula into a neat sample of isopropyl-l-(*m*-bromo-*p*-pisopropoxyphenyl)propionate (1.58 g, 4.79 mmol) in a 50 mL round-bottom flask. The resulting pale yellow solution was stirred for 15 mm at 22 EC. Tributyl(vinyl)tin (1 .54 mL, 5.27 mmol, 1.1 equiv) was then added dropwise to the reaction mixture through a syringe. The flask was equipped with a condenser and heated at 110 °C for 12 h. As the reaction progressed, a shiny mirror-like film of $Bu_3SnBr$ salts was gradually deposited on the walls of the flask. After

pooled and washed with 500 mL of a saturated solution of sodium chloride. Drying over $MgSO_4$ and concentration in vacuo afforded 355 mg (1.52 mmol, 91%) of a light yellow solid which proved to be >98% pure as judged by $^1H$ NMR spectroscopy (400 MHz). If necessary, the acid could be further purified by silica gel chromatography (TLC $R_f$ = 0.31 in 3:2 hexanes:$Et_2O$). It is recommended that the above procedure be followed with care since the product is quite prone to acid-catalyzed polymerization of the styrene moiety. Rapid, uncontrolled addition of the acid or acidification in the absence of $Et_2O$ can result in complete loss of the product to polymerization. IR (NaCl): 2979 (m), 2935 (w), 2860 (w), 2760 (w), 1686 (s), 1600 (s), 1243 (s). $^1H$ NMR (500 MHz, $CDCl_3$): δ 11.26 (br, lH, $CO_2H$), 7.32 (d, $J$= 2.3 Hz, 1H, aromatic CH), 7.06-7.00 (m, 2H, aromatic CH and $ArCHCH_2$), 6.81 (d, $J$ = 8.5 Hz, 1H, aromatic CH), 5.72 (dd, $J$ = 17.8, 1.5 Hz, lH, $ArCHCH_2$), 5.23 (dd, $J$ = 11.0, 1.5 Hz, 1H, ArCHCH2), 4.50 (septet, $J$ = 6.1 Hz, lH, $(CH_3)_2CHOAr$), 2.90 (dd, $J$ = 8.0, 7.6 Hz, 2H, $CH_2CO_2iPr$), 2.67 (dd, $J$ = 8.0, 7.6 Hz, 2H, $ArCH_2$), 1.34 (d, $J$ = 6.2 Hz, 6H, $(CH_3)_2CHOAr$). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 178.78, 153.77, 132.13, 131.88, 128.40, 127.87, 126.29, 114.48, 113.99, 70.99, 35.80, 29.88, 22.19. HRMS Calcd for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1257. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.71; H, 7.68.

**Example 11: Synthesis of Tetraallylsilane (27).** A 250 mL 2-neck flask equipped with a condenser and addition funnel was charged with freshly prepared allylmagnesium bromide in $Et_2O$ (92.3 mL of a 0.95 M solution, 87.7 mmol, 4.1 equiv). $SiCl_4$ (2.45 mL, 21.4 mmol) was slowly added to the solution of Grignard reagent through the addition funnel in 20 mL of $Et_2O$ at 22 °C over the course of 1 h. After 12 h of reflux at 35 °C, the reaction was cooled to 0 °C and quenched with 10 mL of a saturated solution of ammonium chloride. The mixture was diluted with water (200 mL) and $Et_2O$ (100 mL) and transferred to a separatory funnel. The organic layer was collected and the aqueous layer was washed with 2 x 150 mL of $Et_2O$. The organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo into a colorless oil. This material was passed through a small plug of silica in hexanes (TLC $R_f$ = 0.9 in hexanes) and

hexanes). The product was recovered as a colorless oil (2.11 g, 3.56 mmol, 90%). IR (NaCl): 3077 (w), 2954 (m), 2913 (s), 2876 (m), 1630 (m), 1418 (w), 1250 (s), 1153 (m), 1034 (w), 990 (w), 932 (w), 893 (s), 844 (s), 698 (w), 629 (w). $^1$H NMR (400 MHz, $CDCl_3$): δ 5.78 (ddt, $J$ = 16.8, 10.2, 8.2 Hz, 4H, $CH=CH_2$), 4.87-4.79 (m, 8H, $CH=CH_2$), 1.51 (d, $J$= 8.2 Hz, 8H, $SiCH_2CH=CH_2$), 1.32 (m, 8H, $SiCH_2CH_2CH_2Si$), 0.62-0.53 (m, 16H, $SiCH_2CH_2CH_2Si$), -0.02 (s, 24H, $Si(CH_3)_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 135.21, 112.47, 23.49, 19.93, 18.55, 17.54, -3.52. HRMS Calcd for $C_{32}H_{67}Si_5$: 591.4089 (M-H)+. Found: 591.4072. Anal. Calcd for $C_{32}H_{68}Si_5$: C, 64.78; H, 11.55. Found: C, 64.98; H, 11.55.

**Example 13: Synthesis of $Ar(CH_2)_2CO_2(CH_2)_3Si(Me)_2(CH_2)_3SiL_4$ (29).**

$Si[(CH_2)_3Si(Me)_2CH=CH_2]_4$ (28) (587 mg, 0.989 mmol) was weighed into a 50 mL round-bottom flask and dissolved in 10 mL of THF. This solution was treated by cannula with freshly prepared 9-BBN (527 mg, 4.69 mmol, 4.74 equiv) in 10 mL of THF. After 12 h of stirring at 22 °C, 10 mL each of $H_2O_2$ (30% wt. solution in water), 2 M NaOH, and ethanol were added. The mixture was then allowed to stir an additional 12 h at 22 °C. Water (100 mL) and $Et_2O$ (100 mL) were added and the organic layer was removed. The aqueous layer was washed with 2 x 100 mL of $Et_2O$. The combined organic layers were dried over $MgSO_4$ and filtered. Removal of volatiles gave a crude oil that was purified by silica gel chromatography (TLC $R_f$= 0.36 in EtOAc). $^1$H NMR analysis (400 MHz) indicated that the product contained minor impurities (including cyclooctadiol) which made characterization of the material difficult. Thus, the crude product was carried directly into the next step. The tetraol was transferred to a 25 mL round-bottom flask, dissolved in 15 mL of $CH_2Cl_2$, and cooled to 0 °C. 1-(*p*-isopropoxy-*m*-vinylphenyl)propionic acid (**26**) (1.02 g, 4.35 mmol, 4.4 equiv), EDC (912 mg, 4.76 mmol, 4.8 equiv), and DMAP (61 mg, 0.50 mmol, 0.50 equiv) were then directly added in succession to the mixture as solids. The resulting mixture was stirred for 4 h and quenched with 2 mL of a 10% citric acid solution. Additional water was added (200 mL) and the aqueous layer was washed with 3 x 100 mL of $Et_2O$. The combined organic layers were washed with 1 volume each of a

gradient elution (1:1 hexanes:$CH_2Cl_2$ to 2:3 hexanes:$CH_2Cl_2$ to 1:3 hexanes:$CH_2Cl_2$ to 100% $CH_2Cl_2$). Finally, the column was flushed with $Et_2O$, at which point the product elutes (brown band). Solvent removal afforded a dark brown crystalline solid (637 mg, 0.194 mmol, 87%). IR (NaCl): 2927 (s), 2852 (s), 1955 (w), 1733 (s), 1684 (w), 1610 (w), 1582 (w), 1488 (m), 1447 (m), 1417 (w), 1385 (m), 1296 (w), 1247 (m), 1222 (m), 1204 (m), 1134 (m), 1104 (m), 913 (w), 891 (w), 849 (m), 774 (w), 735 (m), 702 (w). $^1$H NMR (400 MHz, $CDCl_3$): 6 17.38 (d, $J$ = 4.0 Hz, 4H, Ru=CHAr), 7.52 (s, 4H, aromatic CH), 7.46 (d, $J$ = 8.8 Hz, 4H, aromatic CH), 6.98 (d, $J$ = 8.8 Hz, 4H, aromatic CH), 5.23 (septet, $J$ = 6.2 Hz, 4H, $(CH_3)_2CHOAr$), 4.03 (t, $J$ = 7.1 Hz, 8H, $CO_2CH_2$), 3.03 (t, $J$ = 7.7 Hz, 8H, $ArCH_2CH_2CO_2$), 2.64 (t, $J$ = 7.7 Hz, 8H, $ArCH_2CH_2CO_2$) 2.32 (m, l2H, PCH), 2.20-1.20 (m, 136H, $CO_2CH_2CH_2CH_2Si(Me)_2$, $SiCH_2CH_2CH_2Si(Me)_2$, and $P(CH(CH_2)_5)_3$), 1 79 (d, $J$ = 6.2 Hz, 24H, $(CH_3)_2CHOAr$), 0.60-0.52 (m, 16H, $CH_2Si(Me)_2CH_2$), 0.50-0.45 (m, 8H, $Si(CH_2)_4$),-0.03 (s, 24H, $Si(Me)_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 279.24, 172.60, 151.29, 143.79, 134.69, 129.42, 122.51 (d, $J_{OC}$= 5.9 Hz), 113.19, 75.50 (d, $J_{OC}$ = 7.8 Hz), 67.27, 36.36, 35.67 (d, $J_{PH}$ = 24.4 Hz), 30.14, 29.73, 27.80 (d, $J_{PH}$ = 10.7 Hz), 26.33, 23.26, 22.14, 20.14, 18.58, 17.56, 11.26, -3.33. $^{31}$P NMR (162 MHz, $CDCl_3$): δ59.17 (s, $PCy_3$). LRMS Calcd for $C_{156}H_{264}Cl_8O_{12}P_4Ru_4Si_5Na_2$ (M+2Na)+: 3331.2. Found: 3331.8. Anal. Calcd for $C_{156}H_{264}Cl_8O_{12}P_4Ru_4Si_5$: C, 57.05; H, 8.10. Found: C, 56.80; H, 8.00.

**Example 15: Synthesis of [(4,5 - dihydrolMES) $Cl_2$ Ru = CH-o-O-i-$PrC_6H_3(CH_2)_2C00(CH_2)_3Si(Me)_2(CH_2)_3Si]_4$** (formula 31). The unmetallated dendrimer (29) (227mg, 0.148 mmol, 1.0 equiv) was weighed into a 25 mL round-bottom flask and dissolved in 15 mL of $CH_2Cl_2$. (4,5-dihydrolMES)$(PCy_3)Cl_2$Ru=CHPh (3) (606 mg, 0.714 mmol, 4.8 equiv) and CuCl (72.0 mg, 0.731 mmol, 4.9 equiv) were added directly to this solution as solids. The mixture was stirred for 2 h at 22 °C, during which time the original purple solution turned a dark green/brown color. The following work-up procedures were conducted in air using reagent grade solvents. The mixture was concentrated at reduced pressure and passed through a short column of silica gel using a gradient elution (100% $CH_2Cl_2$ to 4:1 hexanes:$Et_2O$ to 1:1 hexanes:

**Example 17: Representative Experimental Procedure for RCM Catalyzed by Dendritic [$(PCY_3)Cl_2Ru$=CH-*o*-0-*i*-$PrC_6H_3(CH_2)_2C00(CH_2)_3Si(Me)_2(CH_2)_3Si]_4$ (formula 30).** Tosyl amide (32) (250 mg, 0.995 mmol, 1.0 equiv) and dendritic catalyst (30) (43.9 mg, 0.0140 mmol, 0.0 14 equiv) were weighed into a 50 mL round-bottom flask. The flask was equipped with a reflux condenser, evacuated, and filled with an atmosphere of argon. The vessel was charged with $CH_2C1_2$ (20 mL, 0.05 M) and submerged into an oil bath preheated to 45 °C. The reaction was stirred for 15 minutes, at which point TLC analysis indicated completion of the reaction. Removal of the solvent in vacuo afforded a dark brown oil that was purified by silica gel chromatography (100% $CH_2C1_2$), affording 33 as a white solid (219 mg, 0.983 mmol, 99%). The column was then flushed with 100% $Et_2O$ to recover the dendritic catalyst as a brown solid residue (46.2 mg, 0.0141 mmol, 100%). The recovered catalyst was transferred directly into a new flask for a subsequent reaction. As discussed above, Ru recovery on the dendrimer could be quickly analyzed upon inspection of the $^1$H NMR (400 MHz) spectrum. Integration of the benzylic methylene protons at 3.03 ppm (metal-occupied sites) and 2.88 ppm (metal-vacant sites) provided a ratio of 88:12 respectively.

**Example 18: Experimental Procedure for RCM Catalyzed by Dendritic [(4,5-dihydrolMES)C12Ru=CH-*o*-0-*i*-$PrC_6H_3(CH_2)_2COO(CH_2)_35i(Me)_2(CH_2)_3$ Si]4 (formula 31).** Diene (11) (32.7 mg, 0.233 mmol, 1.0 equiv) was weighed into a 25 mL round-bottom flask and dissolved in 5 mL of $CH_2C1_2$ (0.05 M). Dendritic catalyst 31 (12.4 mg, 0.00366 mmol, 0.0 16 equiv) was added as a solid and the solution was allowed to stir at 22 °C. TLC analysis after 2 h indicated completion of the reaction. Work-up procedures proceeded in air with reagent-grade solvents. The mixture was concentrated at reduced pressure and passed through a short plug of silica gel in 100% $CH_2C1_2$, affording (12) (20.4 mg, 0.1819 mmol, 78%) as a colorless oil (TLC $R_f$= 0.25 in 4:1 hexanes:$Et_2O$). The catalyst was then flushed off of the column with 100% $Et_2O$ affording 12.3 mg (0.00363 mmol, 99%) of a green solid. Ru recovery on the dendrimer was assessed using $^1$H NMR spectroscopy (400 MHz). Integration of the isopropoxy methine proton

mixture consisted of > 98% pure cycloolefin (no catalyst or byproduct thereof could be detected). (3) No filtration step was required to isolate the product. The reaction mixture was simply removed with a Pasteur pipette, the glass sample was washed with $CH_2Cl_2$ , and fresh substrate was added.

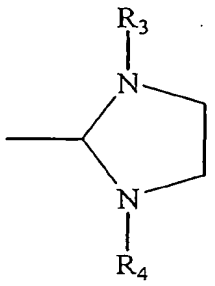
Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for this purpose, and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention as described by the appended claims.

7. The composition of claim 6 wherein $R_1$ and $R_2$ each is Cl.

8. The composition of claim 1 wherein a, b, c, and d each comprises H or a lower alkyl group.

9. The composition of claim 1 wherein Y comprises a 4,5-dihydroimidazol-2-ylidene.

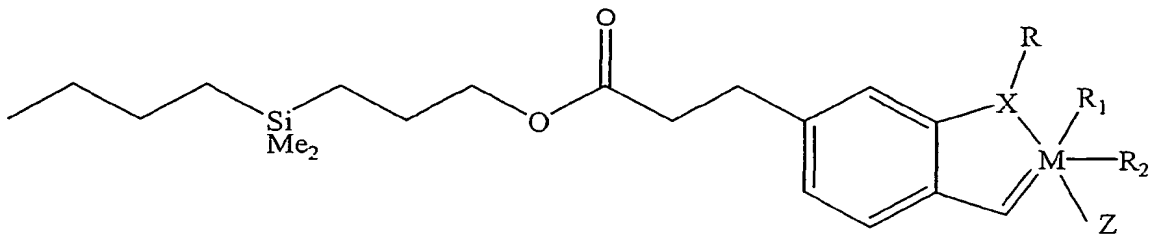
10. The composition of claim 9 wherein Y comprises a tricyclic aromatic ring structure having the following structure:




wherein $R_3$ and $R_4$ each comprises an aromatic ring moiety.

11. The composition of claim 10 wherein $R_3$ and $R_4$ comprise both comprise 2,4,6-trimethylphenyl (mesityl) moieties.

12. The composition of claim 1 comprising the following structure:




wherein:

M comprises a transition metal;

X comprises O, S, N or P;

R comprises an alkyl, alkenyl, alkynyl, aryl, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxy carbonyl, alkylamino, alkylthio, alkylsulfonyl, alkylsulfinyl; each optionally submitted with an alkyl, halogen, aryl or heteroaryl moiety;

$R_1$ and $R_2$ each comprises, or together comprise, an electron withdrawing group; and

Z comprises Y or a phosphinc group.

15. The composition of claim 14 wherein A is silicon.

16. The composition of claim 14 wherein M is a transition metal.

17. The compositon of claim 14 wherein M is ruthenium

18. The composition of claim 14 wherein X is O.

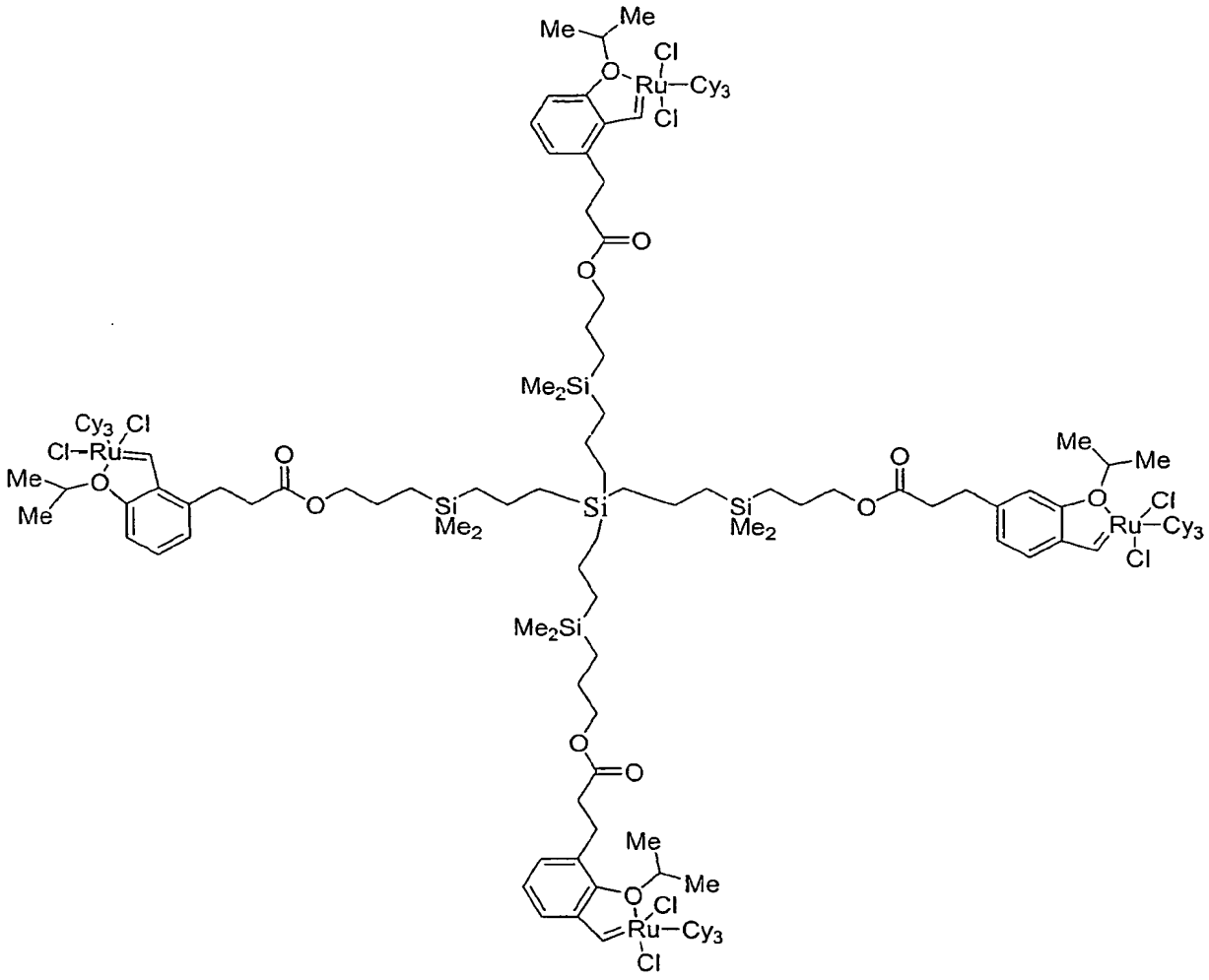
19. The composition of claim 14 wherein R is a lower alkyl group.

20. The composition of claim 19 wherein R is isopropyl.

21. The composition of claim 14 wherein $R_1$ and $R_2$ each is a halogen.

22. The composition of claim 21 wherein $R_1$ and $R_2$ each is Cl.

28. The composition of claim 14 comprising the following structures:



or

33. The transition metal catalyst of claim 32 wherein the substituent is alkylldimethylsilylcholride.

34. A compositon of claim 1 wherein the said catalyst is capable of chemically bonding to a substrate surface.

35. A composition of claim 30 wherein the substrate is a porous or a non-porous solid phase.

36. A compositon of claim 30 wherein the substrate is glass, metal, non-metal, ceramics, rubber or a polymeric material.

37. A compostion of claim 30 wherein the substrate is part of a containing vessel.

38. A composition of claim 37 wherein the containing vessel is a chemical reactor.

39. A method of immobilizing the transition metal catalyst of claim 1 comprising the steps of

i) reacting the said catalyst with a chemical coupling agent under conditions to form an adduct with said catalyst so as to render it capable of attachment to a substrate surface, and

ii) contacting said adduct with a substrate or a substrate surface under conditions to cause said adduct to become chemically bound to said substrate surface through covalent chemical bonding, ionic bonding, non-ionic interaction, or combinations thereof.

40. A method of claim 39 wherein the catalyst is a transition metal catalyst capable of reacting with a chemical coupling agent that is chemically bonded to a substrate surface.

41. A method of claim 40 wherein the chemical coupling agent comprises a compound containing at lcast one alkyl halosilanes, akenyl halosilanes, alkoxy halosilanes, aryloxy halosilanes and aryl halosilanes, akyl and cycloalkyl halides, alkenyl and cycloalkenyl halides,

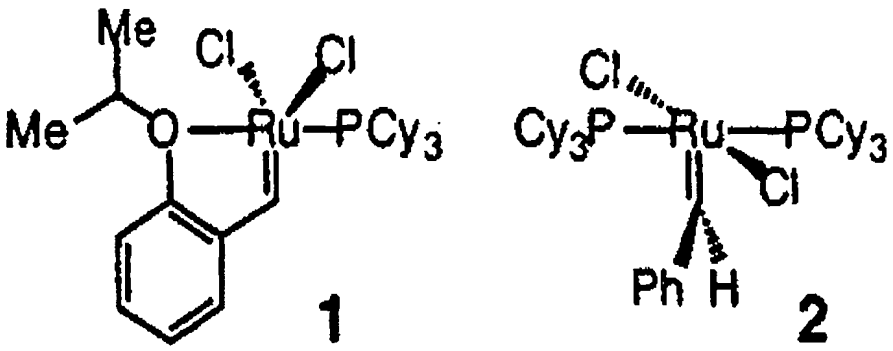
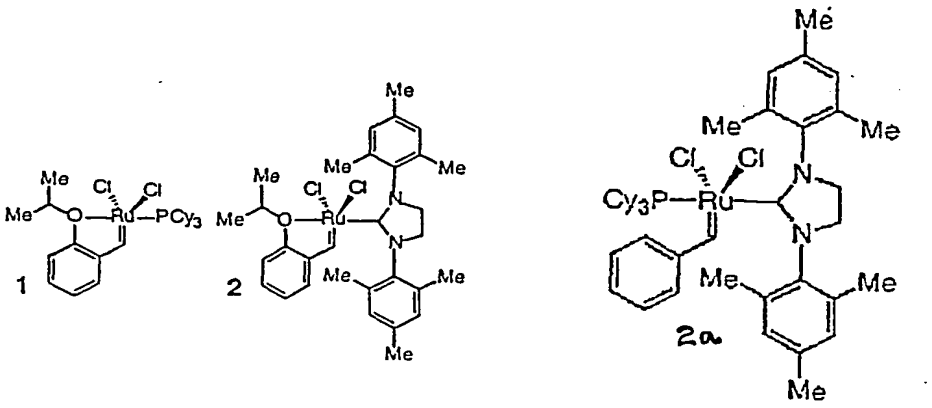



**Figure 1**


Me
Cl
Cl
Me
O
Ru
PCy3
1
Me
Cl
Cl
Me
O
Ru
N
N
Me
Me
Me
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2
Me
Me
Me
Cl
Cl
Cy3P
Ru
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N
Me
Me
Me
2a

**Figure 3**

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(54) Title: RECYCLABLE METATHESIS CATALYSTS

(57) Abstract: Hyghly active, recoverable and recyclable transition metal-based metathesis catalysts and their organometallic complexes including dendrimeric complexes are disclosed, including a Ru complex bearing a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene and styrenyl ether ligand. The heterocyclic ligand significantly enhances the catalytic activity, and the styrenyl ether allows for the easy recovery of the Ru complex. Derivatized catalysts capable of being immobilized on substrate surfaces are also disclosed. The present catalysts can be used to catalyze ring-closing metathesis (RCM), ring-opening (ROM) and cross metatheses (CM) reactions, and promote the efficient formation of various trisubstituted olefins at ambient temperature in high yield.

# INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X, P | GESSLER et al. Synthesis and metathesis reactions of a phosphine-free dihydroimidazole carbene ruthenium complex. Tetrahedron Letters, 16 december 2000, Vol. 41, No. 51, pages 9973-9976, particularly compound 6 on page 9974. | 1-13 |
| X, P | RANDL et al. Highly Selective Cross Metathesis with Acrylonitrile Using a Phosphine Free Ru-Complex. Synlett, 2001, No. 3, pages 430-432, particularly compound 3. | 1-13 |